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Parameters of RO process design

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The design of RO system starts with the ultimate project objective: consistent production of a design flow of product water at a required quality. The selection of process parameters is influenced by type of feed raw and design range of water quality parameters: dissolved species composition and concentration, fluctuation of water temperature and turbidity. The direct design parameters of the RO membrane unit, such as an average permeate flux rate and system recovery rate, are based on type of raw water source and projected feed water quality. The optimization of values of design process parameters, within the recommended ranges, requires understanding the relation between system operating conditions and stability of membrane performance. The average permeate flux rate should be within the range that would not accelerate membrane fouling. The recovery rate should be below the value that would result in excessive saturation limit of the sparingly soluble salts in the concentrate. There are additional process parameters that should be considered. The design process begins with evaluation of feed water quality.

15.1 Feed water composition

The potential sources of wastewater that require salinity reduction are:

- Ground water contaminated by agricultural activity
- Ground water contaminated by industrial activity

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- Municipal wastewater
- Land fill leachate

The composition of ground water, which is contaminated by agricultural activity, is representative of local brackish water, usually with the addition of high concentration of nitrate, contributed through an excessive use of fertilizers. As the source is ground water, the concentration of suspended solids is usually low. Therefore, configuration of RO systems applied to treat this type of water sources is the same as configuration of systems applied for reduction of salinity of regular brackish waters, i.e. the pretreatment is minimal. Description of configuration of ground water reclamation system is provided in Chapter 22. Examples of commercial plants data and design.

Nature of industrial contaminants presented in the ground water is usually related to the past industrial operation in the area. Ground water remediation, using RO technology is a feasible technology for this purpose, if the contaminant species are ionized and general salinity reduction of the water source is also required. If the contaminants are organic and neutral, and salinity reduction is not required, other treatment methods rather than RO are generally more effective.

Vast majority of wastewater reclamation systems treat water that originates from municipal wastewater reclamation plants. In addition to municipal sources, industrial effluent could contribute some of the inflow. Depending on the predominant type of local industry, these influents could include metals, heavy load of natural organics or synthetic compounds. At majority of locations, the municipality has the authority to limit the type, quantity and concentrations of industrial waste that could be discharged to the sanitation district. Local regulations frequently force industrial facilities to treat their waste streams prior to discharge to the municipal sewage network. The treatment applied at the sanitation district usually includes solids screening and some form of biological nutrients reduction (BNR) process. In some cases iron or aluminum based coagulants are added for additional reduction of phosphates (phosphorus) concentration. Prior to RO membrane unit, the so called "secondary effluent" from the sanitation district, is filtrated through microfiltration or ultrafiltration membranes, as described in chapters 3–6. The membrane filtration pretreatment process does not alter the basic composition of the secondary effluent but drastically reduces concentration of suspended solids, including reduction of bacteria and viruses.

Another configuration of wastewater treatment process: membrane bioreactors, produce effluent that is of similar quality as produced by BNR followed by membrane filtration. The MBR effluent could be used, without additional filtration step, as a feed to RO membrane unit.

The composition of tertiary effluent (obtained after membrane filtration) reflects the composition of potable water that could show significant variability between different locations [1–8]. The salinity of tertiary effluent could be higher by 10–30% than the local potable water. Dissolved constituents specific to wastewater are DOC, metals, nitrogen, ammonia and phosphorous based compounds. Table 15.1. provides example of concentration range of typical constituents of a secondary effluent after MF/UF membrane filtration.

The concentration of nitrate is depend on the extend of denitrification and nitrification processes conducted at the sanitation district. As it will be discussed latter, it is beneficial in the secondary effluent, designated for RO processing, to maintain ammonia concentration of about 5 ppm or above.

15.2 Indicators of RO feed water quality

The primary indicators of fed water quality for RO applications are Silt Density Index (SDI) and turbidity. Membrane manufacturers usually define values of these two indicators as part of membrane warranty terms. Secondary indicators,

TABLE 15.1

Example of composition and concentration ranges of constituents in the municipal tertiary effluent (membrane filtration effluent).

Parameter	Units	Concentration
Turbidity	NTU	01.–0.5
pH		6.0–80
Conductivity	S/cm	700–2000
TOC	mg/l	5–15
Ammonia	mg/l	0–20
Chloride	mg/l	60–380
Nitrate	mg/l	5–60
Fluoride	mg/l	0.5–2.0
Sulfate	mg/l	50–110
Calcium	mg/l	30–60
Sodium	mg/l	90–350
Alkalinity (as CaCO ₃)	mg/l	50–250
Silica (as SiO ₂)	mg/l	7–10
Phosphate (as PO ₄)	mg/l	1–15

such as concentration of suspended particles, TOC and concentration of sparingly soluble salts, guide system designer to define process parameters: average permeate flux and system recovery rate.

The SDI is determined in the process of measurement of the rate of filtration of specified volume of water through a filter of defined porosity [9]. The SDI is calculated according to Eq. 15.1.

$$SDI = 100\% \times (1 - t_1/t_2)/Dt \tag{15.1}$$

where t_1 is the initial time required for filtration of specified volume of filtrate (usually 500 ml), t_2 is the time required for filtration of the same volume, measured after elapsed time of Dt (usually $Dt = 15$ min).

The measurement of filtration rate is conducted at constant water pressure, usually ~ 2 bar (30 psi). The schematic configuration of SDI measuring device is shown in Fig. 15.1.

The determination of SDI and relation of the SDI value to concentration of suspended solids is based on formation of cake deposit on the surface of the filter between two measurements of filtration time initially (t_1) and after 15 minutes of continuous filtration of feed water through the filter (t_2). If the concentration of suspended solids is low the plugging of the filter will not be significant and t_2 will be similar to t_1 . Therefore, SDI value will be low (Eq. 15.1). Otherwise, t_2 will be much higher than t_1 , increasing the SDI value.

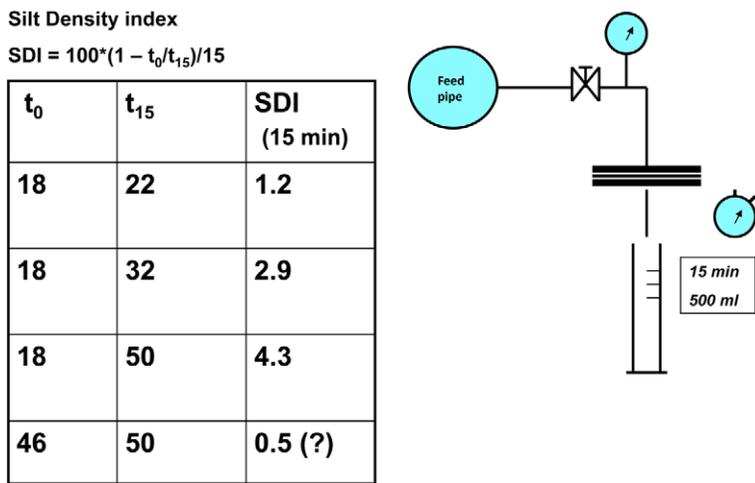


FIG. 15.1 Schematic configuration of device for measurement of SDI.

According to Eq. 15.1, the maximum value of SDI, for time interval of 15 min ($Dt = 15$ min) between two filtration rate measurements, could be only 6.7. Some RO membrane manufacturers advertise maximum allowable SDI value of feed water as $SDI = 5$. However, it is common understanding that for reliable operation of membrane elements, the feed water SDI has to be much lower, preferably below the value of 3. Figs. 15.2–15.4 shows scanning electron microscopy (ESM) images of surfaces of filters used for determination of SDI. Fig. 15.2 shows the SEM image of a surface of a clean filter. Figs. 15.3 and 15.4 are SEM images of filters after determination of SDI. Fig. 15.3 corresponds to

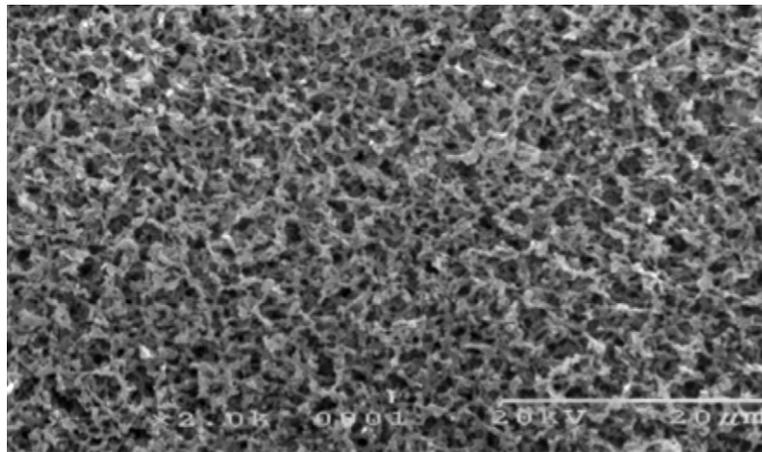


FIG. 15.2 SEM picture of a clean filter pad (reference). Magnification $\times 2000$.

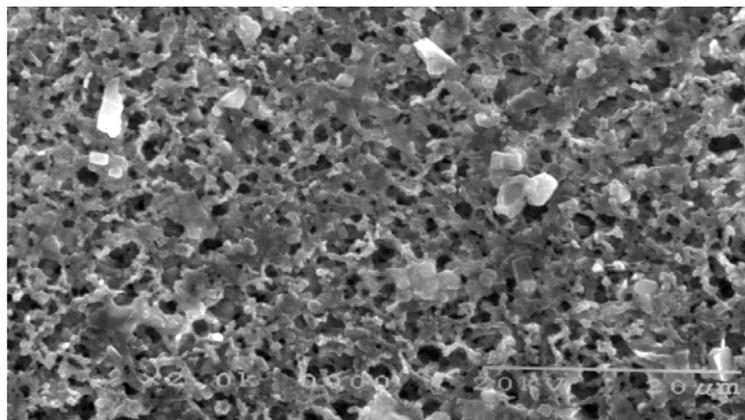


FIG. 15.3 SEM picture of a filter pad after SDI determination. $SDI = 2.2$. Magnification $\times 2000$.

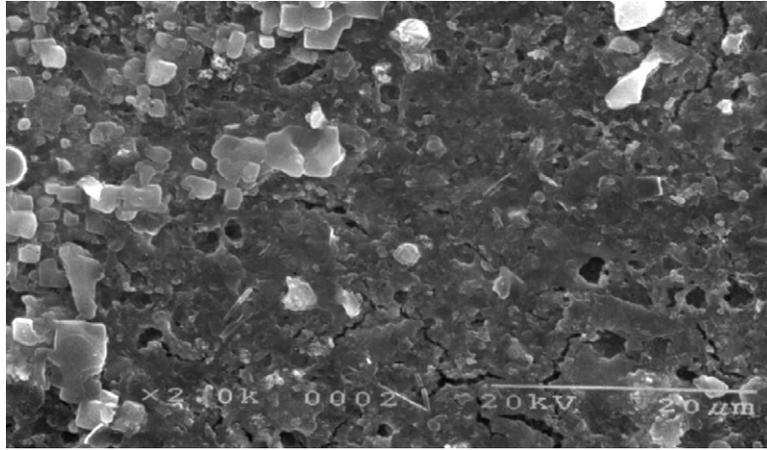


FIG. 15.4 SEM picture of a filter pad after SDI determination. SDI = 4.8.
Magnification $\times 2000$.

filtration of water with SDI of 2.2 and Fig. 15.4 corresponds to filtration of water with SDI of 4.8. As indicated by images in Figs. 15.3 and 15.4, the deposit on filter surface that corresponds to SDI of 4.8 is significantly higher than deposit formed during filtration of feed water with SDI of 2.2.

It has been suggested by authors of one of the recent publications [10], that the increase of SDI values for given water sample, corresponds to geometric ratio of increase of concentration of suspended solids.

The SDI is very sensitive indicator of presence of suspended solids in water. However, the SDI readings could vary significantly with type and size of suspended particles present in the water and type of material of the filter pad used for SDI determination. The required equipment for determination of SDI is very simple and procedure easy to conduct at field conditions. However, both the accuracy and reproducibility of results are not very satisfactory.

The deficiencies of SDI were somewhat corrected with introduction of Modified Fouling Index (MFI) by Schippers and Verdouw [11]. The determination of MFI is based on measurement of declining rate of filtration versus volume of filtrate. The MFI is determined as a slope of this graph. The MFI is linear with concentration of particles in the feed water. However, the test is difficult to perform manually and automatic measuring equipment is necessary [12, 13]. One of the disadvantages of both SDI and MFI is that the determination process involves dead-end filtration through the polymeric filter vs. tangential flow of feed water over the membrane surface in RO membrane element [14]. There-

fore, the decline of filtration rate measured during fouling index determination cannot be directly correlated with RO membrane fouling and applied to model the potential decline of permeability.

Some field measurements of SDI of UF filtrate provided unexpectedly high results [15]. The speculation is that the presence of organics and formation of micro air bubbles may affect the filtration rate through the 0.45 micron filter pad in addition to presence of suspended particles.

In spite of the above deficiencies, SDI is universally adopted as a primary indicator of feed water quality in RO systems.

Determination of SDI takes about 25–30 min. Common approach is to conduct manual SDI measurements once per shift or once per day. RO plants employing automatic measuring equipment conduct measurements more frequently.

The secondary feed water quality indicator, used in RO applications is turbidity. Turbidity results, usually expressed as nefelometric turbidity units (NTU), are determined through measurements of intensity of light scattered by suspended particles in a water sample [16]. Turbidity sensor could provide continuous measurement of feed water turbidity. Turbidity results are sensitive to quantity of colloidal particles, their size and shape. Past attempts to correlate between SDI and turbidity results, even for the same site, demonstrate very weak relations [17]. These two water quality indicators correlate to the number and size of suspended particles differently. However, the general rule is that feed water with SDI in the range of 2–3 has a corresponding turbidity below 0.1 NTU, usually at 0.05 NTU range.

It can be expected that with increasing number of wastewater reclamation system utilizing reverse osmosis process, new feed water quality indicator will be adopted that will provide better correlation between feed water quality parameters and propensity of membrane to fouling. Potential feed water quality indicators may include number of particles in a specific size range, values of TOC, UV adsorption and others. Meanwhile, the SDI is still relayed on as a primary indicator for determination of effectiveness of pretreatment and suitability of feed water for RO processing.

15.3 Membrane fouling

During the membrane fouling process, performance of membrane elements changes due to formation of deposits on membrane surface or inside of feed–brine channel. Fouling affects membrane elements performance. The

symptoms of fouling are decrease or increase of water permeability, increase or decrease of salt rejection and increase of pressure drop across the RO unit. Later stages of uncontrolled fouling could result in structural damage of membrane or membrane element. List of fouling factors encountered in RO applications is included in Table 15.2.

The specific membrane fouling process that could be of concern in desalination system in wastewater reclamation will depend on application type and composition of feed water. Summary of more frequent potential fouling processes, grouped by application type, is provided in Table 15.3.

Fouling can be prevented or mitigated by reduction of concentrate of the foulant in the pretreatment step, adjustment of feed water pH, addition of scale inhibitor, operation at average flux rate and recovery that would not result in high fouling rate. The configurations of pretreatment system, applied in wastewater reclamation systems, are discussed in Chapters 3–10.

15.3.1 Oxidative degradation of membrane performance

The sensitivity of membrane performance to presence of strong oxidants was known at the very onset of development composite polyamide membrane.

TABLE 15.2
Summary of membrane fouling categories and their symptoms.

Fouling factor	Initial fouling stage effect	Advanced fouling stage effect	Potential membrane damage
Exposure to strong oxidants	Some permeability and salt passage decline. Initially in the lead element(s)	Increase of permeability and significant increase of salt passage	Irreversible damage of membrane barrier
Colloidal matter	Some increase of pressure drop. Initially in the lead element(s).	Significant increase of pressure drop, some decline of permeability and increase of salt passage	Element telescoping and extrusion of brine spacer. Membrane barrier damage
Dissolved natural organic matter (NOM)	Some permeability and salt passage decline.	Moderate decline of permeability, same salt passage decline	None

continued

TABLE 15.2 *continued*

Summary of membrane fouling categories and their symptoms.

Fouling factor	Initial fouling stage effect	Advanced fouling stage effect	Potential membrane damage
Biological matter	Some increase of pressure drop. Some permeability and salt passage decline. Initially in the lead element(s).	Significant increase of pressure drop. Some permeability and salt passage decline.	Element telescoping and extrusion of brine spacer. Membrane barrier damage
Inorganic scale	Some increase of pressure drop. Some permeability decline. Initially in the tail element(s).	Severe increase of pressure drop. Some permeability decline and salt passage increase.	Severe blockage of feed channels
Petroleum products, also oil and grease	Significant permeability decline in the lead element(s). Small effect on salt passage	Severe decrease of permeability. Small effect on salt passage	None at low concentration. At high concentrations barrier integrity damage
Composite foulants (organics + colloids)	Some increase of pressure drop. Some water permeability decline. Initially in the lead element(s).	Significant increase of pressure drop. Significant permeability decline and some salt passage increase.	Significant blockage of feed channels. Element telescoping. Membrane barrier damage
Sharp edged, micron size particles in feed water	Gradual salt passage increase	Significant salt passage increase	Cuts and holes in membrane barrier
Prolonged exposure to very high pH (> 12)	Increase of water permeability and salt passage	Significant increase of water permeability and salt passage	Chemical damage of membrane barrier material
Prolonged exposure to very low pH (< 2)	Initial decrease of water permeability and salt passage	Significant decrease of water permeability	Chemical damage of membrane barrier material
Low concentration of organic solvents	Gradual decrease of water permeability, increase of salt passage	Significant decrease of water permeability, increase of salt passage	Swelling of membrane barrier and eventually chemical damage

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TABLE 15.3

Summary of fouling potential, more frequent fouling processes for various wastewater reclamation applications.

Application type	Fouling process	Likely culprit
Ground water reclamation	Membrane scaling	High concentration of silica, calcium sulfate, calcium carbonate, barium sulfate in the concentrate
	Particle induced cuts of membrane barrier	Presence of mineral particles in feed water.
Reclamation of industrial streams	Any of the fouling processes listed in Table 15.2.	Potentially any industrial waste constituent present in the feed water
Reclamation of municipal wastewater	Scaling	High concentration of calcium phosphate, calcium carbonate in the concentrate
	Blocking of feed channels	High concentration of colloidal matter in the feed water.
	Adsorption of organics	Present of high concentration of NOM in the feed water
	Biofouling	Insufficient concentration of chloramines in the feed water
	Oxidation of membrane barrier	Presence of free chlorine (insufficient ammonia concentration) in the feed water

The early tests of exposure of polyamide membrane to free chlorine, indicated limited initial stability followed up by a significant decline of salt rejection [18]. The subsequent screening study conducted at University of California, Los Angeles [19], corroborated with previous observation. However, it signaled out chlorine dioxide, as a disinfectant that potentially could be used in RO systems equipped with polyamide membranes. Latter laboratory evaluation [20] identified 1 ppm of chlorine dioxide concentration as a threshold level. Above 1 ppm the decline of salt rejection was very significant. At feed concentration of chlorine dioxide below 1 ppm, the rejection decline was relatively small, from the initial value of 97.8% to a value of 96.0% after 200 days of operation.

The above results should be view in a correct perspective:

1. The membrane stability tests were conducted with feed solution of NaCl, ClO₂ and buffer in deionized water. It is known that presence of transition metals in feed water at trace concentration could accelerate oxidation of membrane barrier.
2. Even this “small” decrease of salt rejection from 97.8% to 96.0%, actually corresponds to salt passage increase of almost 100%. Doubling of permeate salinity within operation period of about seven months would not be an acceptable level of membrane performance stability in commercial desalination systems.

RO membrane operating in municipal wastewater reclamation systems are exposed to high concentration of organics in the feed water that rapidly adsorb on membrane surface during the initial stage of operation. This condition enables use of chloramines to prevent membrane biofouling. With the presence of chloramines in the feed water in the concentration range of 2–4 ppm, salt passage increases at a rate of about 100% within 3–5 years of operation. This is an acceptable rate for majority of applications.

Use of chloramines for other RO application, almost always results in very rapid salt passage increase [21]. The possible reason for slower effect of chloramines on salt rejection change in wastewater application is presence of organic layer on membrane surface. Most likely, this organic layer reacts with chloramines, decreasing its concentration at the membrane surface. In addition, the organic matter present in the feed, plugs pinholes and other defects in membrane barrier, effectively reducing the salt transport.

Presently, the use of chloramines in RO systems desalting tertiary municipal effluent is a common operational procedure. The operating conditions are designed to maintain chloramines level at 2–4 ppm in the feed to the membrane unit. If level of ammonia in feed water is too low to produce sufficient concentration of chloramines, ammonia could be added, usually in the form of ammonium chloride, adjacent to chlorine (or hypochlorite) injection point.

15.3.2 Colloidal fouling

Colloidal fouling is not a common phenomenon in membrane wastewater reclamation systems. Ground water sources, even these contaminated by agricultural or industrial effluents, usually have very low concentration of colloidal matter. Water undergoes natural filtration during passage through a sand layer in the underground aquifer.

Membrane filtration of the secondary municipal effluent, used as pretreatment, prior to RO, practically removes all colloidal matter. The other municipal source, effluent from membrane bioreactor (MBR), is practically of the same quality as tertiary effluent after MF or UF filtration.

Presence of colloidal fouling, in RO units operating in municipal wastewater reclamation systems, is usually a result of lack of integrity of membrane barrier in the pretreatment system. In some cases, colloidal particles could form as a result of precipitation from a saturation solution of scale forming salts [22]. Another possible source of colloidal particles could be coagulant used in the membrane filtration system [23]. The coagulant particles could pass through micropores of MF membrane or form in the RO system as the feed volume is reduced and concentration of soluble metal ions increases into a saturation range.

Presence of colloidal matter in RO feed could result in very rapid permeability decline. Colloidal matter, mixed with organics, forms on the membrane surface a very dense layer of low permeability. Colloidal particles could also become a crystallization centers for sparingly soluble salts that are at saturation, and induce formation of scale. Use of membrane filtration as a pretreatment step, prior to RO, prevents in most cases colloidal fouling of RO membranes.

15.3.3 Fouling by organic matter

The municipal and industrial wastewater contains high and variable concentrations of organics. Some fraction of the organics is in a form of suspended colloidal particles. Majority of these will be removed during the pretreatment step of membrane filtration. According to one published classification [24], the wastewater effluent organic matter (EfOM) is a mixture of organics of different origin. The EfOM contains natural organic matter (NOM) derived from drinking water sources, synthetic organic compounds (SOC) contributed by domestic and industrial use, disinfection by products (DBP) created during disinfection process and wastewater treatment and soluble microbial products (SMP) produced during biological processes of wastewater treatment. This mixture of organic compounds, determined as dissolved organic carbon (DOC) could be composed of polysaccharides, proteins, aminosugars, humic and other organic acids and synthetic organic compounds.

The reduction of concentration of dissolved organics by MF or UF filtration is not significant. Some reduction, up to about 30% could be achieved if coagulation is applied prior to membrane filtration. The reduction mechanism is through adsorption of organic compounds on coagulant particles and subsequent removal by membrane filtration.

In majority of cases, the effect of dissolved organics on membrane performance is reduction of water permeability, associated with some decrease of salt passage (improvement of salt rejection).

The extend of water permeability decline and the decline rate depends on composition of organic mixture in the feed, characteristics of membrane surface and composition and ionic strength of feed water [25–27]. In RO reclamation units with well functioning pretreatment, the long term water permeability decline is expected to be in the range of 30%–40%. Usually, the decline irate is high at the startup, reaching 10%–20% and then levels off with time [28]. Accordingly, the feed pumping system has to be designed to provide sufficient feed pressure to compensate for the above decline of permeability over time. Except for permeability decline, fouling of RO membranes by dissolved organics, usually does not result in other adverse effect on membrane performance parameters (build up of feed channel pressure drop or increase of salt passage).

In some isolated cases organic scale inhibitor, added to the feed to prevent scaling, could react with coagulant and foul the membrane. For example, one reported case refers to interaction of aluminum based coagulant with scale inhibitor [29]. RO systems treating industrial effluents, could result in even higher rate of flux decline rate then listed above. Some dissolved industrial organics may cause membrane swelling. Membrane manufacturers should be consulted regarding potential compatibility issue with industrial type feed constituents.

15.3.4 Biofouling

Biofouling, which is the phenomena of bacterial film formation in RO systems, could represent a serious operation problem. Bioufouling manifest itself in increase of feed channel pressure losses and productivity decline [30]. Systems contaminated with established bacterial grow are very difficult to clean and restore to the original performance level.

The assumption is that every body of water contains microorganisms in equilibrium with the local nutrients supply. The water born microorganisms easily attached themselves to the surfaces in the RO systems and form colonies. The attachment to the surfaces is through excretion of extra cellular polymeric substance (EPS), composed mainly of polysaccharides. On wetted surfaces, the microbiological cells and surrounding EPS form biofilm, which can grow at rapid rate if sufficient nutrients and energy are available. The structures of biofilms are not uniform, depending on type of microorganisms and environmental conditions: pH, temperature, flow velocity, age and variety of other parameters.

The general knowledge about biofilms mechanism formation and their control is still developing. More recent research approach, under umbrella of “biofilm ecology” utilizes genetic tests to monitor biofilms growth and study microorganisms diversity [31].

The biofouling occurrence is limited mostly to RO systems processing surface water [32] or ground water from shallow wells. Majority of RO systems processing well water experience little or no biofouling. Number of procedures have been developed to identify condition of availability of nutrient and to monitor biofilm grow [33–35].

RO treatment of municipal effluents represents unique situation of high biofouling potential of RO feed water and development of effective way of controlling microorganisms population [36]. In the past, municipal effluents were processed using cellulose acetate membranes. Therefore, it was a common practice to chlorinate RO feed water to prevent microorganisms grow. Due to presence of ammonia and high concentration of organics in the effluent the free chlorine was converted to chloramines. Today, almost all RO systems treating municipal effluents use composite polyamide membranes. Based on field experience it has been established that in wastewater applications salt rejection of composite membranes, in presence of chloramines concentration of 2–4 ppm, is sufficiently stable to provide 3–5 years effective membrane life. The above range of chloramines concentration is also sufficient to effectively mitigate membrane biofouling in RO unit. If secondary effluent is completely nitrified, then addition of ammonia containing compound to RO feed water, as discussed in Chapter 15.3.1, will be required to enable formation of sufficient concentration of chloramines.

15.3.5 Inorganic scale

The concerns for potential of scale formation in RO systems are related to the very nature of the RO process: removal of water from the feed stream and increase of concentration of the ions present in the feed water.

During the RO process concentration of all constituents increases due to reduction of the feed water volume. This increase of concentration is function of permeate recovery (Eqs. 11.9 and 11.10). There is possibility for some of the dissolved constituents to nucleate and precipitate, if the concentration product of salt forming ions exceeds its solubility product: K_{sp} . For a given salt of composition $C_m A_n$ in equilibrium of solid phase salt (S) with dissolved ions, the K_{sp} is defined as:

$$C_m A_n(S) = mC^{+n} + nA^{-m} \quad (15.1)$$

$$K_{sp} = [C^{+n}]^m [A^{-m}]^n \quad (15.2)$$

$$SI = [C]^m [A]^n / K_{sp} \quad (15.3)$$

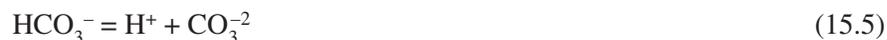
where C stands for cation and A for anion, m and n are valency coefficients. Brackets [] indicate molar concentration of a given ion in solution. SI is the saturation index, indicating excess concentration of a given salt in comparison to its saturation value.

The K_{sp} is determined through measurement of ions concentrations in solution at saturation conditions (in equilibrium with a solid phase of a given salt). K_{sp} has a specific value for each salt and it is function of temperature and ionic strength of the solution.

In wastewater reclamation systems, the salt of concern is mainly calcium carbonate, less frequently calcium phosphate. In some isolated cases, potential for precipitation of barium sulfate has to be considered.

Calcium carbonate is the most common scaling constituent in natural occurring waters and also in wastewater. However, it is also the easiest to control either with pH adjustment or use of scale inhibitor.

In solution, calcium ions are in equilibrium with bicarbonate and carbonate species as shown in the following equations:



At sufficiently high concentrations of Ca^{+2} and CO_3^{2-} , crystallites of $CaCO_3$ could nucleate and form a scale. The calcium carbonate system is quite complex. Saturation conditions are not just function of concentrations of Ca, CO_3 and HCO_3 ions but also influenced by concentration of hydrogen ion (pH) and other ions that contribute to water alkalinity [37].

Attempts to define relations for saturation conditions in potable water networks lead to development of a number of saturation indexes. The calcium carbonate saturation index developed by Langelier [38] for potable water networks has been adopted by RO industry as an indicator of saturation conditions in concentrate stream of brackish water RO systems. The Langelier Saturation Index (LSI) is calculated according to relations:

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$$\text{LSI} = \text{pH} \rightarrow \text{pH}_s \quad (15.7)$$

Where pH I is the actual pH of the water and pH_s is pH that corresponds to saturation concentrations of ions forming calcium carbonate.

$$K_2 = [\text{H}^+] \times [\text{CO}_3^{-2}] / [\text{HCO}_3^-] \quad (15.8)$$

$$K_{\text{sp}} = [\text{Ca}^{+2}] \times [\text{CO}_3^{-2}] = [\text{Ca}^{+2}] \times [\text{HCO}_3^-] \times K_2 / \text{H}_s^+ \quad (15.9)$$

$$\text{H}_s^+ = [\text{Ca}^{+2}] \times [\text{HCO}_3^-] \times K_2 / K_{\text{sp}} \quad (15.10)$$

$$-\log[\text{H}_s^+] = \text{pH}_s = -\log[\text{Ca}^{+2}] - \log[\text{HCO}_3^-] + \log [K_{\text{sp}}/K_2] \quad (15.11)$$

$$\text{LSI} = \text{pH} \rightarrow \text{pH}_s = \text{pH} - \text{pCa} - \text{pAlk} + \text{pK} \quad (15.12)$$

Where K_2 is second dissociation constant to carbonic acid (H_2CO_3), K_{sp} —solubility constant of calcium carbonate at given pH and temperature. Other parameters represent molar concentrations of relevant species in the solution.

Few years after introduction by Langelier the saturation index was modified [39] to account for ionic strength in a form of correction factor proportional to water salinity.

$$\text{pH}_s = (9.3 + A + B) - (C + D) \quad (15.13)$$

$$\text{where: } A = (\text{Log}_{10} [\text{TDS}] - 1) / 10 \quad (15.14)$$

$$B = -13.12 \times \text{Log}_{10} (^\circ\text{C} + 273) + 34.55 \quad (15.15)$$

$$C = \text{Log}_{10} [\text{Ca}^{+2} \text{ as } \text{CaCO}_3] - 0.4 \quad (15.16)$$

$$D = \text{Log}_{10} [\text{alkalinity as } \text{CaCO}_3] \quad (15.16)$$

The parameter A is related to ionic strength of the solution. The value of A increases with increase of salinity. Parameter B reflects the changes of calcium carbonate solubility and changes of equilibrium of carbonic acid dissociation with temperature. The value of B decreases with temperature increase. In practical applications the LSI is either calculated using computer programs or monograms based on pH and composition of concentrate stream. Water solution has potential for CaCO_3 scaling at $\text{LSI} > 0$ and it is assumed that saturation prediction using LSI is reliable up to salinity of about 5000 ppm TDS.

For very high water salinity and seawater applications the LSI was modified to account for increased ionic strength by Stiff and Davis [40]. The Stiff and Davis saturation index (SDSI) introduces empirical constant K in calcula-

tions pH_s to account for high ionic strength of seawater concentrates. Stiff and Davis determined value of K experimentally in the high range of ionic strength, that covers salinities encountered in RO seawater applications.

$$\text{SDSI} = \text{pH} - (9.3 + K - \text{pCa} - \text{pAlk}) \quad (15.17)$$

Where pH has the same meaning as in LSI equation and K is a constant found in monograms.

For high salinity solutions (seawater concentrates) the SDSI value is about 1–1.3 units lower than calculated according to the LSI relations. In low salinity applications the values of LSI and SDSI are similar.

Example # 15.1

Calculation of Langelier saturation index

Brackish water system is design to operate at recovery ratio of 80%.

Feed water feed has TDS = 1700 ppm, ionic strength 0.04 and the following concentrations of the relevant ions:

Ca = 300 ppm, $\text{HCO}_3 = 250$, $\text{pH} = 7.3$, $\text{temp} = 25^\circ\text{C}$.

After acidification and pH adjustment to 6.5, $\text{HCO}_3 = 166$ ppm,
 $\text{CO}_2 = 78$ ppm

Concentration factor for 80% recovery rate, $\text{CF} = 1/(1 - R) = 5$

Approximate concentrations in the concentrate:

TDS = 8500 ppm, ionic strength 0.18, Ca = 1500 ppm, $\text{HCO}_3 = 830$ ppm,
 $\text{CO}_2 = 78$ ppm

Calculation of concentrate pH.

$$\text{pH} = \text{pK}_1 + \log ([\text{HCO}_3]/[\text{CO}_2])$$

K_1 is the equilibrium constant of the carbonic acid dissociation reaction. For water temperature of 25 C and dilute solutions K_1 value is 4.2×10^{-7} , $\text{pK}_1 = 6.37$.

Then the concentrate $\text{pH} = 6.37 + \log((830/78) \times (44000/61000)) = 6.37 + 0.89 = 7.26$

Calculation of pHs and LSI

Following equations 15.13–15.16:

$$\text{pHs (feed)} = 9.3 + 0.22 + 2.08 - 2.17 - 2.13 = 7.48$$

$$\text{LSI (feed)} = 6.5 - 7.48 = -0.98$$

$$\text{pHs (concentrate)} = 9.3 + 0.29 + 2.08 - 2.87 - 2.83 = 5.97$$

$$\text{LSI (concentrate)} = 7.26 - 5.97 = 1.29$$

The LSI provides qualitative indication about saturation condition of solution that contains calcium and carbonate ions. The LSI does not enable prediction about quantity of CaCO_3 that could potentially precipitate from solution. The saturation index that provides indication about quantity of CaCO_3 that could precipitate is the calcium carbonate precipitation potential (CCPP). The calculations of CCPP are more laborious than calculations of LSI [41]. The calculations of CCPP are usually conducted using specialized computer programs.

The values of the LSI and CCPP are only indicative precipitation potential. The actual precipitation through primary or secondary precipitation (in presence of nucleation centers) depends on number of environmental parameters and thermodynamically preferred solid phase as discussed in more recent publication on the subject of calcium carbonate precipitation [42]. According to this publication, solubility limit of anhydrous forms of calcium carbonate is not the onset of precipitation. Solubility of hydrated forms of CaCO_3 , amorphous calcium carbonate, monohydrate calcium carbonate and hexahydrate calcium carbonate, which have higher solubility than the anhydrous calcium carbonates represent the more realistic limit of concentrations in RO applications.

The Modified Langelier Saturation Index (MLSI), based on solubility equilibrium of monohydrate calcium carbonate, has solubility limit about one unit higher than LSI. The modified solubility limits have been tested at laboratory conditions but have yet to be confirmed in field conditions.

The results [42] also indicate slow rate of the nucleation process, that is in the range of above 10 min, much longer than 1–2 min feed water residence time in the membrane inlet of the RO system.

Short residence time of feed–concentrate stream in the membrane array, as illustrated in Example 15.4, is probably another condition that allows operation of RO unit with solutions at saturation without precipitation.

Example #15.2

Two stage RO unit with seven elements per vessel. Number of membrane elements operating in series = 14. Membrane area per element 40m^2 (430ft^2). Number of membrane leaves per element 30. Element length 1 m (39.4"). Feed channel height 0.8 mm (0.031"). Assume open cross section of feed channel = 0.8 (80%) of nominal due to presence of feed spacer. Membrane unit operates at recovery rate of 80%, average permeate flux rate $20.4\text{ l/m}^2/\text{hr}$ (12 gfd) = $0.0204\text{m}^3/\text{m}^2/\text{hr}$.

Calculate approximate average residence time of feed water in the RO unit.

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Feed channel with (length of membrane leaves) = $40 \text{ m}^2 / (1 \text{ m} \times 30 \times 2) = 0.67 \text{ m}$

Feed channel cross section = $0.8 \times 0.67 \text{ m} \times 0.8 \text{ m} / 1000 = 0.00043 \text{ m}^2$

Total cross section of feed channels in element = $(30 - 1) \times 0.00043 \text{ m}^2 = 0.0125 \text{ m}^2$

Feed flow to the unit = $(14 \times 40 \text{ m}^2 \times 0.0204 \text{ m}^3/\text{m}^2/\text{hr}) / 0.8 = 14.28 \text{ m}^3/\text{hr}$

Feed flow velocity = $14.28 \text{ m}^3/\text{hr} / 0.0125 \text{ m}^2 / 3600 \text{ sec} = 0.3 \text{ m/sec}$

Concentrate flow from the unit = $(1 - 0.8) \times 14.28 \text{ m}^3/\text{hr} = 2.85 \text{ m}^3/\text{hr}$

Concentrate flow velocity = $2.85 \text{ m}^3/\text{hr} / 0.0125 \text{ m}^2 / 3600 \text{ sec} = 0.06 \text{ m/sec}$

Average flow velocity = $0.06 \times 1 \ln(0.3/0.06) / (1 - 0.06/0.3) = 0.12 \text{ m/sec}$

Average residence time in membrane unit = $14 \times 1 \text{ m} / 0.12 \text{ m/sec} = 117 \text{ sec} \sim 2 \text{ min.}$

The above residence time is short as compared with slow rate of crystals grow. However, If some constituents are in a metastable state of oversaturated solution, in presence of crystallization centers the secondary nucleation and massive precipitation could be instantaneous. The flow distribution through feed channel is not uniform and some stagnant areas exist. At these areas, the residence time could be significantly longer.

The saturation relation of calcium sulfate is simpler to calculate than the one for calcium carbonate. For RO calculations it is assumed that its solubility depends only on concentrations of calcium and sulfate ions, temperature and ionic strength. The effect of ionic strength on solubility of calcium sulfate is quite significant as shown in the following example of calculations of saturation indexes (SI) of CaSO_4 for water salinities corresponding to brackish and seawater RO systems:

Example #15.3

For CaSO_4 : $K_{sp} = (\text{temp}/25)^{0.152} \times 1.8 \times 10^{-3} \times \text{IS}^{0.75}$

Brackish water system

R = 75%, TDS of concentrate = 4000 ppm, IS = 0.07

Ca = 900 ppm, $\text{SO}_4 = 2400$ (concentrations in concentrate)

$K_{sp} = 2.5 \times 10^{-4}$

SI = $([900/40000] [2400/96000]) / 2.5 \times 10^{-4} = 2.25$

Seawater system

R = 50%, TDS of concentrate = 80,000 ppm, IS = 1.60

$\text{Ca} = 900 \text{ ppm}$, $\text{SO}_4 = 6000 \text{ ppm}$ (concentrations in concentrate)

$K_{\text{sp}} = 2.6 \times 10^{-3}$

$\text{SI} = ([900/40000] [6000/96000])/2.6 \times 10^{-3} = 0.54$

In the example above the product of calcium and sulfate ions concentrations in solution is much higher in concentrate stream of the seawater system as compared to the brackish system. However, due to the differences of ionic strength, the calcium sulfate is above saturation level in the brackish system and below saturation in the seawater system.

In wastewater reclamation systems calcium sulfate practically never reaches a saturation potential due to limits of calcium and sulfate ions concentrations in potable water supply. In some isolated cases barium sulfate could be a recovery rate limiting constituents. Solubility of barium sulfate is five orders of magnitude lower than solubility of calcium sulfate.

Another constituent that sometimes can present problem in RO applications is silica. Silica concentration in wastewater effluents will depend on its concentration in potable water, which is low at majority of locations. Silica can be present both in colloidal and reactive (soluble) form [43].

In the past, the safe limit of silica concentration in concentrate was considered as being about 140–170 ppm (as SiO_2). In the last decade a new scale inhibitors were introduced that are effective in maintaining much higher concentration of silica in solution. Some suppliers of these specialty inhibitors claim safe limits for silica concentration as high as 300 ppm. When treating brackish sources with significant silica concentration an extreme caution should be exercised with maintaining the designed recovery rate as silica scale is very difficult to remove from membrane elements.

Beside calcium carbonate, the major scaling compound of concern in RO wastewater reclamation systems is calcium phosphate. Calcium phosphate presence is almost uniquely associated with household or industrial effluents at various concentrations. In majority of RO system treating municipal effluents concentration of phosphates is low and does not result in membrane scaling.

The chemistry of calcium–phosphate compounds is quite complex and precipitants of calcium and phosphates can be formed as number of chemical formulations of different solubility [44, 45]. The prevailing assumption is that most likely scale forming compounds are: calcium phosphate dihydrate (DCPD-Brushite) and Tricalcium phosphate (TCP). At locations where phosphates concentration is high, formation of scale during RO operation could be prevented by using scale inhibitors or acidification. The effectiveness of scale inhibitor in prevention of formation of calcium phosphate scale is not well doc-

umented. Results of one experimental work of evaluation of commercial scale inhibitors [46] indicate very low effect on rate of scale formation. Reduction of feed pH is very effective in prevention of phosphate scaling. The solubility limits for DCPD were developed experimentally and follows the equation [54] that provides maximum value for Ca and P product in solution according to concentration of hydrogen ion (pH):

$$Ca \times P = 10^{3.85} + 10^{11.55} \times [H^+] \tag{15.18}$$

For TCP an empirical relation for calculation of saturation index was developed by BETZ Company:

$$\text{Index} = \text{pH} - \frac{11.755 \log(\text{Ca}) \log(\text{PO}_4) - 2 \log(f)}{0.65} \tag{15.19}$$

where

pH = pH of the concentrate

Ca = Calcium concentration in the concentrate, ppm CaCO₃

PO₄ = Phosphate concentration in the concentrate, ppm

t = Water temperature, °C

Positive value of the phosphate saturation index indicates that scaling could occur. Scaling can be controlled by use of scale inhibitor or acidification of feed water.

Table 15.4 provides values of concentrate pH required for maintaining phosphate saturation index below the threshold value of 1 at the recovery rate range of 75%–85% for the concentration of calcium and phosphate in the feed water and concentrate as listed below.

TABLE 15.4
Controlling phosphate scaling through pH adjustment.

Parameter	Feed water	Concentrate @ R = 75%	Concentrate @ R = 80%	Concentrate @ R = 85%
pH	8.1	6.8	6.5	6.1
Ca, ppm	300	1200	1500	2000
P, ppm	3	12	15	20
PO ₄ , ppm	9.2	36.7	45.9	61.2
Phosphate saturation index (Eq. 15.19)	-0.5	0.74	0.74	0.72

However, acidification of RO feed, required to prevent formation of calcium phosphate scale, could be very expensive if significant quantity of acid would be required due to high alkalinity concentration.

Example #15.4

Calculation of quantity of acid required to prevent calcium phosphate scaling.

For concentration of bicarbonate ion $[\text{HCO}_3^-]$ in feed water is 300 ppm as

CaCO_3 , calculate quantity of sulfuric acid required:

- To reduce feed pH from 8.1 to 7.
- To bring pH of concentrate from feed pH of 8.1 to the pH values listed in Table 15.4.

Feed water temperature 25 C.

Values of K_1 , K_2 and K_w are: 4.45×10^{-7} , 4.42×10^{-11} and 9.17×10^{-15}

Calculate concentration of $[\text{CO}_2]$, $[\text{CO}_3^{2-}]$, $[\text{H}^+]$ and $[\text{OH}^-]$ in feed according to the following equations:

$$[\text{CO}_2] = \frac{[\text{H}^+]}{K_1} [\text{HCO}_3^-] \quad (15.20)$$

$$[\text{CO}_3^{2-}] = \frac{K_2}{[\text{H}^+]} [\text{HCO}_3^-] \quad (15.21)$$

$$[\text{H}^+] = 10^{\text{pH}} \quad (15.22)$$

$$[\text{OH}^-] = 10^{(\text{pH} - \text{p}K_w)} \quad (15.23)$$

According to the above relations, the concentrations (mol/l) are:

$$[\text{H}^+] = 7.94 \times 10^{-9}$$

$$[\text{OH}^-] = 1.15 \times 10^{-6}$$

$$[\text{HCO}_3^-] = 6.00 \times 10^{-3}$$

$$[\text{CO}_2] = 1.07 \times 10^{-4}$$

$$[\text{CO}_3^{2-}] = 3.34 \times 10^{-5}$$

The concentration of total alkalinity (A_T) and total carbonate species (C_T) are calculated according to equations 15.24 and 15.25. The assumption is made that contribution of phosphate species to alkalinity can be neglected.

$$A_T = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] \quad (15.24)$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (15.25)$$

Accordingly

$$\begin{aligned} A_T &= 6.07 \times 10^{-3} \\ C_T &= 6.14 \times 10^{-3} \end{aligned}$$

Acidification to adjust pH has no effect on C_T . Therefore, new concentration of CO_2 can be calculated according the Eq. 15.26

$$[\text{CO}_2] = \frac{C_T}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}} \quad (15.26)$$

$$[\text{CO}_2] = 1.13 \times 10^{-3} \text{ mol/l (49.7 ppm)}$$

Concentrations of other components of the alkalinity are calculated according to equations 15.20 – 15.23.

The total feed alkalinity at pH = 7 is:

$$\begin{aligned} A_{T1} &= 5.02 \times 10^{-3} \\ C_{T1} &= 6.14 \times 10^{-3} \end{aligned}$$

Quantity of sulfuric acid required to acidify feed water from pH of 8.1 to pH of 7.0 is

$$(A_T - A_{T1}) \times \text{Eqv H}_2\text{SO}_4 = (6.07 \times 10^{-3} - 5.02 \times 10^{-3}) \times 49000 = 51 \text{ mg/l (as 100\%)}$$

The next step is to estimate what should be the feed pH required for a required pH of the concentrate.

An approximate value can be derived by calculation of concentrate pH for a designed recovery rate.

The calculations of alkalinity species and pH of the concentrate are based on the assumption that CO_2 is not rejected by the membrane, i.e. concentration of CO_2 in feed and concentrate are the same, and the other dissolved species are rejected completely.

Accordingly concentration of carbonate species in concentrate, C_{TC} will be:

$$C_{TC} = (C_{T1} - [\text{CO}_2]) / (1 - R) + [\text{CO}_2] \quad (15.27)$$

For a concentration of carbonate species at feed water pH of 7.0 and recovery rate $R = 80\%$

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$$C_{TC} = (6.14 \times 10^{-3} - 1.13 \times 10^{-3}) / (1 - 0.80) + 1.13 \times 10^{-4} = 3.03 \times 10^{-2} \text{ mol/l}$$

Substituting the value of C_{TC} and $[CO_2]$ in equation 15.26, concentration of $[H^+]$ and pH_C of the concentrate can be calculated.

$$pH_C = 7.8$$

Accordingly, for concentrate pH, listed in Table 15.4, the required feed pH should be about 0.8 units lower for the determined pH of the concentrate.

Following the calculations of alkalinity and quantity of sulfuric acid for feed acidification, shown in the first part of this example, the quantity of sulfuric acid for required pH of the concentrate, starting with feed pH of 8.1, is given in Table 15.5.

The results listed in Table 15.5 indicates that cost of acidification, to prevent calcium phosphate scaling, could be quite significant and should be considered in the early stages of evaluation of project feasibility.

The solubility of sparingly soluble salts is affected by ionic strength.

The K_{sp} values (at 25 C and for low ionic strength solutions) or concentration limit of common salts that could form scale in RO systems are listed in Table 15.6

The potential for formation of calcium sulfate scale and blocking of feed channels in the spiral wound element is demonstrated in the following example:

Example #15.5

For the following concentration of Ca and SO_4 in the concentrate calculate scaling potential of calcium sulfate:

$$[Ca] = 1000 \text{ ppm} = 0.025 \text{ mol}$$

$$[SO_4] = 2400 \text{ ppm} = 0.025 \text{ mol}$$

$$K_{sp} = 2.25 \times 10^{-4}$$

$$\text{Saturation } [Ca] = [SO_4] = (2.25 \times 10^{-4})^{1/2} = 0.015 \text{ mol}$$

$$\text{Excess } [Ca] = [SO_4] = 0.010 \text{ mol}$$

$$\text{MW } CaSO_4 = 40,000 + 96,000 = 136,000 \text{ mg/l}$$

$$\text{Excess } [CaSO_4] = 0.010 \text{ mol} = 0.010 \times 136,000 = 1,360 \text{ mg/l}$$

The RO system operates at 80% recovery rate. At average flux of 26l/m²-hr, 7 elements per vessel the concentrate flow in the last element is: $26 \times 36.8 \times 7 \times (1 - 0.80) / 0.80 = 1674 \text{ l/hr}$

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TABLE 15.5

Quantity of sulfuric acid required to maintain concentrate pH below the threshold value of saturation index of calcium phosphate.

Recovery rate, %	75	80	85
Required concentrate pH	7.0	6.7	6.3
Required feed pH	6.2	5.9	5.5
Dosing rate of H ₂ SO ₄ , ppm (100%)	173	219	260
Contribution to product water cost, \$/m ³ at sulfuric acid cost of \$500/t	0.087	0.109	0.130

TABLE 15.6

K_{sp} or concentrations limit of scale forming compounds common to RO.

Compound	Formula	K _{sp} or concentration limit, (ppm)
Calcium sulfate	CaSO ₄	2.5 × 10 ⁻⁵
Barium Sulfate	BaSO ₄	2.0 × 10 ⁻¹⁰
Tricalcium Phosphate	Ca ₃ (PO ₄) ₂	2.8 × 10 ⁻³⁰
Calcium Phosphate Dihydrate	CaHPO ₄ × 2H ₂ O	2.2 × 10 ⁻⁷
Calcium Carbonate	CaCO ₃	LSI < 0, S&DSI < 0
Reactive Silica	H ₄ SiO ₄	(120–160 ppm)

Potential CaSO₄ deposit = 1674 × 1.36 = 2276 g/hr = 2.28 kg/hr

Assuming specific density of CaSO₄ = 4g/cm³, volume of excess CaSO₄ that could precipitate is RO element is (2.28 × 1000)/4 = 570 cm³/hr.

Free volume of feed channels in SW element is:

100 cm × 100 cm × 0.075 cm × 20 = 15000 cm³ (about 50%)

The above calculations shows that at the saturation conditions scale could lead in a short time to complete blockage of tail elements.

Potential for scale formation is extremely important issue in brackish and wastewater reclamation applications. At some locations, it may determine the maximum recovery rate for the RO systems. Due to variability of water compositions and limited level of understanding of the relevant salt solutions systems at saturation in RO conditions, it is quite difficult to make accurate predictions

about scaling. RO industry adopted limits for individual salts based literature data and some field experience (Table 15.4). Due to lack of accurate analytical models, developed for RO applications, these limits include significant safety margins.

Manufacturers and suppliers of scale inhibitors are continuously introducing new scale inhibitors that enable operation at higher levels of concentrations than those initially proposed by membrane manufacturers. So far, the experience with the subsequent products introduced over the years was quite positive. Seldom could any problems of scale formation be related to malfunction of scale inhibitor if applied according to manufacturer specifications. Scale inhibitors prevent scale formation by retardation of the nucleation process of scale forming crystals. The mechanism of prevention of crystal growth is either through threshold effect, crystal structure distortion, dispersion or sequestration.

The dosing rate of scale inhibitor is determined by supplier of chemicals based on feed water composition and recovery rate. Feed water analysis should include information on concentration of iron. High concentration of iron containing compounds in concentrate may reduce effectiveness of some scale inhibitors. Required concentration of scale inhibitor seldom exceeds 10 ppm of active ingredient in the concentrate stream.

15.4 System recovery rate

Permeate recovery ratio of an RO unit, which is the rate of conversion of feed water to permeate affects process design and the economics of the RO/NF systems. The flow rate of water that flows through the system is uniquely determined by the design recovery ratio. Therefore, flow rate of the raw water supply system, capacity of the pretreatment system, sizes of the high pressure pumps, feed and concentrate manifolds are all functions of the system recovery rate. Higher recovery rate allows smaller equipment size and lower cost. On the operating side, in RO systems treating low salinity feed, operation at higher recovery rate usually results in lower pumping energy requirement.

The total pumping energy (E_t) in RO system is composed of the following components:

$$E_t = E_{rw} + E_{pr} + E_{hp} + E_{pr} \quad (15.28)$$

where: E_{rw} is energy of raw water pumping, E_{pr} is hydraulic energy losses in the pretreatment system, E_{hp} is energy required by motor of high pressure feed pump and E_{pr} is energy required for pumping of product water.

The additional energy, sometimes required for pumping of the concentrate, is usually supplied by the discharge energy of the concentrate stream.

The energy of pumping (E_p) is defined as:

$$E_p = C \times Q \times H \times r / (hp \times hm) \quad (15.29)$$

$$E_p = C \times Q \times P / (hp \times hm) \quad (15.30)$$

where: C is conversion constant for units system used, Q is flow rate, H is hydraulic head, r is fluid density, hp is pump efficiency, hm is motor efficiency and P is pressure differential developed by pump.

Accordingly, the specific of the RO process, in kWhr per unit volume of permeate, is function of recovery rate, R:

$$E_p = C \times Q \times P / (hp \times hm \times P) \quad (15.31)$$

According to the equation 11.16, hydraulic losses in the membrane unit (P_d) contribute to the required feed pressure.

$$NDP = P_f - P_{os} - P_p - 0.5 \times P_d \quad (11.16)$$

Higher recovery results in lower feed and concentrate flow rates. Therefore, with increased recovery the pressure drop will decrease (Fig. 15.5) according to Equation 15.32.

$$P_d = A \times Q_{fb}^B \quad (15.32)$$

where P_d is pressure drop, A and B are constants specific for element configuration, Q_{fb} is an average flow rates of feed–concentrate streams

At the high end of recovery rate range, the required feed pressure may actually increase, despite reduction of pressure drop. The increase of feed pressure is due to the increase of an average feed salinity and corresponding osmotic pressure with increased recovery rate (Eq. 11.16). The net effect on feed pressure, by decrease of pressure drop and increase of average osmotic pressure with recovery, will depend on feed salinity.

Due to increased average feed salinity, permeate salinity will be higher at increased recovery rate. In wastewater reclamation systems some increase of permeate salinity at higher recovery rate usually would not present a permeate quality problem if product water is used for aquifer injection or irrigation. In

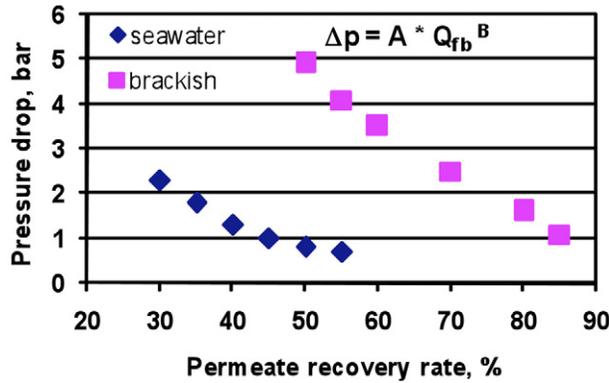


FIG. 15.5 Example of pressure drop in RO unit vs. recovery rate.

cases of industrial use increased permeate salinity may not be acceptable for industrial customers.

The upper limit of recovery rate is determined by concerns of proper system hydraulics and possibility of scale formation.

In order to reduce concentration polarization, membrane manufacturers specify minimum value of the concentrate flow, usually applicable to the elements in last position. Compliance with the minimum concentrate flow requirement may, in some cases, limit the upper value of system recovery. The more stringent limitations are related to scaling concerns. Vendors of scale inhibitors usually help to establish safe recovery range for operation of RO systems with their products. Usual range of recovery rate of RO unit operating in wastewater reclamation applications is 75%–85%.

15.5 Permeate flux rate

Together with recovery rate, permeate flux is very important process parameter that affects permeate quality, fouling rate, system cost and operating cost. System designed for operation at higher flux rate would require lower number of membrane elements, therefore cost of RO trains will be lower.

Operation at higher flux rate requires higher net driving pressure (NDP), which according to Eq. 11.16 would result in higher feed pressure requirement. Therefore, operating cost resulting from cost contribution of energy for process pumping would be higher.

According to Eq. 11.6, increasing permeate flux is associated with reduced concentration of dissolved permeate constituents, due to increased dilution effect at higher rate of permeate flow.

As discussed in chapter 11.11, increasingly higher permeate flux results in faster rate of delivery of feed water constituents (solute) to the membrane surface. The equilibrium concentration at membrane surface will be a net result of convectional delivery to the membrane surface, diffusion flow from the membrane surface and rate of tangential cross flow [47, 48] combined with feed spacer induced mixing. It is postulated, that at some value of flux rate, often designated as “critical flux,” a rapid fouling of membrane surface will occur [49].

The determination of required number of membrane elements in RO unit is based on an average permeate flux rate (see example 11.9). Fig. 11.16 shows schematically variation of NDP along the RO unit. It is evident that permeate flux rate in RO unit will change in parallel to changes of NDP. The fouling rate will depend of rate of delivery of foulants to the membrane surface, which is function of flux rate and their concentrations in the feed water at give position in the system. This local concentration is function of initial concentration in the feed water and the recovery rate.

The concentration profile of foulants in RO unit is opposite to the permeate flux profile. The concentration is low at the feed end of the system and increases with increased recovery rate. In addition, the membrane fouling process is “self regulating.” Increased fouling rate reduces water permeability, which in turn reduces rate of delivery of foulants to the membrane surface.

The average permeate flux rate, in vast majority of membrane units operating in wastewater reclamation systems, is relatively low, in the range of 17–20.4 l/m²/hr (10–12 gfd). Operation of membrane units, in the above range of average permeate flux rate, results in stable long term performance.

The permeability losses due to the fouling are usually in the range of 20%–30%. Small numbers of RO systems, that utilize unique proprietary electromagnetic feed water conditioning, combined with operation at sequence of intermittent flushing, were able to demonstrate stable operation at significantly higher permeate flux rates [50].

15.6 Membrane replacement rate

Membrane longevity is determined by the level of performance over time, stability of water permeability and salt rejection. The formation of fouling layer on membrane surface, abrasive effect of particles in the feed water and

exposure to cleaning chemicals at extreme pH, could eventually change property of membrane barrier and result in performance deterioration. In addition, in wastewater reclamation systems RO membrane elements are operating at condition of continuous exposure to an oxidizing agent: chloramines.

As discussed previously, wastewater reclamation is a unique application where presence of chloramines in feed water does not result in rapid deterioration of salt rejection property of the membrane. Still some increase of salt rejection is encountered [51]. During long term operation of RO units in wastewater reclamation systems, it has been observed a decrease of water permeability with time and a parallel, increase of salt passage [52]. Even in RO systems maintaining a frequent schedule of cleaning procedures, the rate of recovery of permeability decreases with time.

The expected changes of membrane performance are accounted for in calculation of projected operating parameters and performance of RO system by assuming annual increase of salt passage and decrease of permeability.

The approach varies among different membrane manufacturers but it is generally assumed an annual salt passage increase of up to 10% and irreversible permeability decline of 7% per year. For wastewater applications, the permeability decline rate is assumed as being higher than in other RO application. The usual design value is 10%–15% per year of permeability decline.

For salt passage a straight line relations of salt passage increase over time are being calculated in accordance with Eq. 15.33. The retained permeability, after some period of operation, is projected according to the Eq. 15.34. Fig. 15.6 shows changes of membrane performance according to Eqs. 15.33 and 15.34.

$$SP_y = SP_0 \times (1 + SPI)^Y \tag{15.33}$$

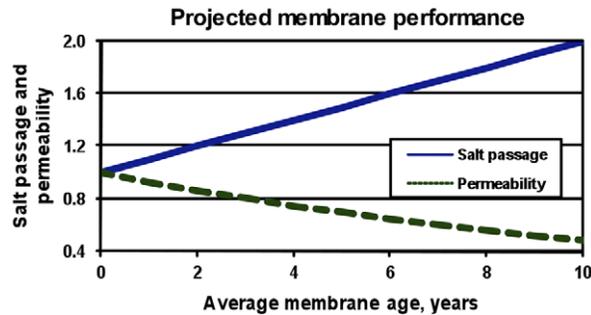


FIG. 15.6 Projected changes of salt passage and water permeability over time.

$$\text{Perm}_y = \text{Perm}_0 \times (1 - \text{Decl})^Y \quad (15.34)$$

Where SP_y is salt passage at the year Y , SP_0 is the initial salt passage and SPI is salt passage increase factor, expressed as a decimal fraction. For the permeability (Perm) the same designations applies.

Accordingly for 3rd year of operation at 10% salt passage increase and 15% permeability decline:

$$\begin{aligned} \text{SP}_3 &= \text{SP}_0 (1 + 0.1) \times 3 = \text{SP}_0 \times 1.30 \\ \text{Perm}_3 &= \text{Perm}_0 (1 - 0.15)^3 = \text{Perm}_0 \times 0.61 \end{aligned}$$

Example # 15.6

RO system utilizes RO membranes elements with nominal specific flux of 4.9 l/m²/hr/bar (0.20 gfd/psi).

System operating parameters:

Feed salinity: 1200 ppm TDS

Permeate salinity: 40 ppm TDS

Recovery rate 80%

Average permeate flux: 19 l/m²/hr (11 gfd)

Permeate pressure 1 bar (14.5 psi)

Pressure drop across the system 3.8 bar (55 psi)

Flux decline: 15% year

Calculate feed pressure at the startup and after projected feed pressure 3 years of operation.

Concentrate salinity

$$C_c = (1200 - 0.80 \times 40) / (1 - 0.80) = 5840$$

Average feed salinity

$$C_{\text{avg}} = (1200 + 5840) / 2 = 3520 \text{ ppm TDS}$$

Average osmotic pressure

$$P_{\text{os}} = 3520 \times 0.00077 = 2.7 \text{ bar (39 psi)}$$

Required NDP according to equation 11.22:

$$\text{NDP}_0 = 19 \text{ l/m}^2\text{/hr} / 4.9 \text{ l/m}^2\text{/hr/bar} = 3.9 \text{ bar (57 psi)}$$

According to equation 11.16, initial feed pressure (P_f) is:

$$P_{f0} = 3.9 + 2.7 \times 0.5 \times 3.8 + 1 = 9.5 \text{ bar (138 psi)}$$

Permeability after three years of operation is:

$$4.9 \text{ l/m}^2\text{/hr/bar} \times (1 - 0.15) = 3.0 \text{ l/m}^2\text{/hr/bar}$$

NDP after three years of operation is:

$$\text{NDP}_3 = 19 \text{ l/m}^2\text{/hr} / 3.0 \text{ l/m}^2\text{/hr/bar} = 6.3 \text{ bar (91 psi)}$$

Feed pressure after three years of operation is:

$$P_{f3} = 6.3 + 2.7 \times 0.5 \times 3.8 + 1 = 11.9 \text{ bar (172 psi)}$$

According to calculations example above, permeability decline of 40% could result in increase of required feed pressure of about 25%.

Figure 15.7 shows relations between feed pressure and rate of membrane fouling in RO system operation at recovery rate of 85%, flux rate of 19 l/m²/hr (11 gfd), feed salinity of 1000 ppm TDS and feed water temperature of 15, 25 and 35°C. Fouling has increasingly higher effect on feed pressure as fouling rate increases and feed water temperature declines.

The useful membrane life is determined by changes of membrane performance and required quality of product water and operating feed pressure. The usual approach is to budget in the operating cost an annual replacement of some fraction of the number of membrane elements in the system. However, for practical reasons the actual replacement is conducted by replacing all membrane elements in a train or desalting stage when system performance deteriorates below the acceptable level in respect of permeate salinity or feed pressure.

Membrane replacement is usually conducted after attempts to restore membrane performance through cleaning have not produced satisfactory results. In some desalination systems, in order to reduce membrane replacement compo-

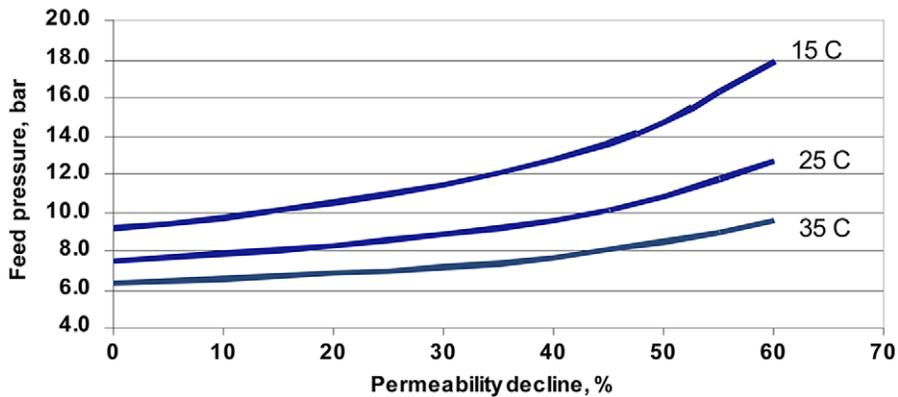


FIG. 15.7 Feed water pressure as function of fouling rate. Feed salinity 1000 ppm TDS, recovery rate 85% and permeate flux 19 l/m²/hr.

ment of the operating cost, an elaborate membrane replacement procedure were developed and successfully implemented [53].

It is seldom the case that performance of all elements would deteriorate uniformly, at the same rate. Therefore, it is obvious that the performance restoration process would be more effective if elements having worst performance would be replaced first.

The problem with implementation of this approach is that it is quite difficult to determine performance of individual elements, when they are in operation in pressure vessel. The salt rejection of individual element can be determined based on conductivity of permeate the element is producing through a “probing” procedure (described in chapter 17). However, determination of permeability requires removal elements from the system and individual testing in a separate RO unit. Afterwards, the elements with satisfactory performance could be returned to operation or used in the next replacement operation.

For projections of long term system performance an estimation of average membrane life is necessary. The estimation is based on assumed (or warranted) membrane replacement rate. An example of calculation of average membrane age is given in table 15.7.

In the above table, the average age is calculated based on setting the membrane replacement event at the beginning of a given year of plant operation. If, for example, the replacement would be conducted at the year end, starting at the end of the first year, then the average membrane age at the end of 5th year would be higher, about 3.75 years. As will be discussed in the following chapters, the average membrane age is used as a parameter for calculation of membrane performance, which eventually is the basis for the terms of system performance warranty.

If the attempts to restore system performance by applying membrane cleaning are not sufficiently successful, the only other alternative is to correct performance through membrane replacement. The fraction of membrane elements that have to be replaced will depend on membrane conditions and required level of system performance.

Table 15.8 demonstrates effect of element replacement on permeate salinity. In this example the system with new elements produced initially permeate salinity of 30 ppm TDS. The upper limit of allowed permeate salinity is 200 ppm TDS. Due to performance deterioration, at the current conditions of the elements in the system, the permeate salinity is 500 ppm TDS. The fraction of the elements to be replaced depends on the target permeate salinity after replacement. Under assumption that new elements will have the same nominal salt rejection as the original load, to restore system to the ability to produce permeate

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TABLE 15.7
Average membrane age table for replacement rate of 15% per year.

Year of operation	0	1	2	3	4	5	Average age
0	100%						0
1	15%	85%					0.85
2	15%	15%	70%				1.55
3	15%	15%	15%	55%			2.10
4	15%	15%	15%	15%	40%		2.50
5	15%	15%	15%	15%	15%	25%	2.75

TABLE 15.8
Membrane replacement for permeate salinity correction.

RO units utilizing membrane elements with nominal 99.5% salt rejection.
Feed salinity 1150 ppm TDS. Recovery rate 85%.
Initial permeate salinity: 30 ppm. Design salinity limit: 200 ppm.
Current permeate salinity: 500 ppm.

Target permeate salinity, ppm TDS	Salt passage relatively to feed salinity, %	Salt passage relatively to average feed salinity, %	Elements to be replaced, %
30	2.7	0.7	100
100	8.7	2.4	74
200	17.4	5.2	52
300	26.1	8.4	30
400	34.8	12.2	9

of the original salinity (30 ppm TDS) all elements in the system will have to be replaced. To bring system in compliance with required permeate salinity of 200 ppm TDS a 52% of elements will have to be replaced.

Table 15.9 demonstrates two options for restoration of productivity in a membrane unit. In this example the system was design to maintain rated capacity at 80% of nominal elements productivity.

Due to excessive fouling the current productivity is only 70%, example A (or 60%, example B). To recover lost productivity, two alternatives are possible: some of the old elements could be replaced with new elements, or number of new elements could be added to the system.

TABLE 15.9

Permeate flow restoration through membrane replacement or addition.

Flux restoration mode	Current capacity, % %, examples A & B	Target capacity, %	Elements to be replaced or added, %
Elements replacement (A)	70	80	33
Elements replacement (B)	60	80	50
Elements addition (A)	70	80	10
Elements addition (B)	60	80	20

The results listed in table 15.9 demonstrate that it is more cost effective, for productivity increase, to add new elements to the system rather than replace some of the old elements. However, with the addition of elements, the membrane area in operation will increase. This will result in increased permeate salinity. The salinity increase will be in proportion to increase of membrane area. Therefore, the option of adding elements can only be implemented if a sufficient permeate quality margin exists.

Option B, when it is possible to implement, would be a less expensive solution. However, this option would require designing of RO trains that would provide number of empty pressure vessels for additional elements. After the membrane unit has been fabricated and constructed, modifications of manifold piping to add pressure vessels is usually not a practical solution.

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